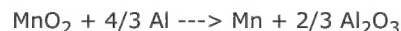


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Manganese thermite based on manganese (II) oxide

I've run many thermite reactions in the past, including [silicon thermite](#) and [titanium thermite](#), as well as many others that I haven't written about, namely iron, chromium, vanadium, cobalt, copper, ferrotitanium, ferrosilicon, ferrochromium, ferrovanadium and copper titanium bronze. But manganese thermite has been the object of many failed attempts, basically up to now.

Those familiar with thermite reactions may wonder what I mean by 'failed' in the manganese thermite context. Well, it isn't my primary objective to put on a good fireworks display, something that any backyard scientist in possession of any of the higher oxides of manganese can attain. The classic manganese dioxide thermite reaction:



is one of the most exothermic pyrometallurgical reactions in the entire series of thermites: its reaction enthalpy (per mol of MnO_2 and at 298 K) is - 597 kJ. That's enough to cause any well proportioned and well ignited mixture of fine manganese dioxide and aluminium powder to cause a dazzling display of extremely high temperature.

And that's precisely the problem with the aluminothermic reduction of MnO_2 (manganese (IV) oxide,  Manganese dioxide): in adiabatic (or near-adiabatic) conditions *it runs far too hot*. The reaction is often described on Internet posts as 'explosive' (although I can assure you that only if the burning mixture is contained - in a bomb like enclosure e.g. - is there a serious risk of an actual explosion in the strict sense of the word). My own experience with MnO_2 -based thermites confirms that these mixtures have a tendency to deflagrate, or 'throw their toys out of their pram'. Often one ends up with a completely empty crucible, with the formed metal and alumina (Al_2O_3 , here also referred to as 'the slag') thrown out of it. Needless to say, if producing small quantities of relatively pure manganese metal is the objective then that objective cannot be attained this way.

The problem becomes clear when comparing the heat generated by the reaction, the heat required to melt both the nascent metal and alumina and bearing in mind the melting points of both the alumina and the manganese metal. Pyrometallurgical extraction of metals from their oxides (or halides) depends on the reaction products to achieve the molten state, so that the metal can separate out from the molten slag/metal mix, much like oil separates out from an oil/water mixture. The melting point of alumina is 2,054 C (3,729 F) and the melting point of manganese is 1,246 C (2,275 F), so basically we need to reach 2,054 C to obtain both the alumina and manganese in molten form and for the slag/metal separation to be able to occur. Below this temperature, powdered metal would be frozen in a powdered, sintered slag pile.

The reduction of MnO_2 with aluminium powder generates as said above about 600 kJ per mol of oxide reduced (at 298 K). Thermochemical data (typically from [NIST](#)) shows that to heat and melt 1 mol of manganese metal to 2,054 C requires about 85 kJ and the heat to melt 1 mol of alumina to 2,054 C requires about 393 kJ (these values include also the actual heats of fusion required). From the reaction equation $\text{MnO}_2 + 4/3 \text{ Al} \rightarrow \text{Mn} + 2/3 \text{ Al}_2\text{O}_3$ can be gleaned that the reduction of 1 mol of manganese dioxide yields one mol of manganese metal and 2/3 mol of alumina, requiring $85 + 2/3 \times 393 = 347$ kJ to reach 2,054 C.

At first glance this is excellent news because in adiabatic conditions (all heat generated by the reaction is used to heat up the reaction products and no heat is lost to the environment - these conditions more or less exist provided the reaction proceeds very quickly, because heat transfer takes time) the reaction produces considerably more heat (600 kJ) than is needed to heat up the reaction products past the melting point of alumina (347 kJ). The manganese dioxide thermite (in more or less adiabatic thermite conditions) will heat up well beyond the minimum requirement of 2,054 C, necessary to obtain slag/metal separation and thus solid reguli of metal after the reacted mass has cooled down.

Unfortunately there's a snake in the grass. Manganese doesn't only have a relatively low melting point, its boiling point is only 2,061 C (3,742 F) and thus only barely higher than the melting point of alumina. Since as we've shown the manganese (IV) oxide thermite reaction to well exceed the melting point of alumina, it's reasonable to assume the reactive mix will reach temperatures that exceed the boiling point of manganese metal (a precise estimate of the end-temperature of such a reactive mix is possible and shows it will in fact exceed 2,500 C, well above the 2,061 C boiling point of manganese).

This then explains why almost no backyard scientists have ever obtained manganese metal from a manganese (IV) oxide based thermite reaction. On one occasion I found tens if not hundreds of fine (sub mm) globules of manganese metal around the reaction crucible: the metal had boiled off and *it really was raining manganese that day!* It also explains why manganese thermite is often referred to (somewhat erroneously) as 'explosive'.

And it begs the question how to run this thermite cooler, so that its maximum end-temperature stays (ideally) in the 2,054 - 2,061 C area...

One fairly obvious way would be to run the thermite in strongly non-adiabatic conditions, in plain English: by cooling it down a lot. But for backyard scientists cooling such a hot object to a fairly narrow window of temperature is easier said than done. Open reaction vessels with extensive cooling fins at the bottom end of the reactor, pre-cooling the reaction mix prior to ignition and such like are possibilities that could be explored but would require in my opinion a great deal of hit-and-miss and costly experimentation.

Using coarser rather than very fine ingredients is also a possibility because heterogeneous reactions tend to run much slower with coarser reagents and this allows the reacting mix to exchange more heat with the environment (assuming an open reactor set-up), thus running cooler. But the relation between mix granulometry and reaction temperature (in non-adiabatic conditions) is complex and hard to establish in a reliable and reproducible way.

Another possibility is the use of heat sinks mixed in with the reagents, prior to ignition. One such heat sink is routinely used by pyrometallurgists and backyard thermite enthusiasts alike: calcium fluoride (CaF_2 , fluorite or fluorspar) has a relatively low melting point (1,402 C or 1,675 F), is completely inert (it doesn't take part in the reaction and doesn't decompose to any appreciable degree) and requires about 166 kJ per mol to melt and heat to 2,054 C. It not only therefore absorbs some of the reaction heat, thereby reducing the end temperature of the mix somewhat but its relatively low melting point also ensures that at the melting point of alumina, molten fluorite is highly fluid (low viscosity) and for that reason is often referred to as a *slag fluidiser*. It also forms a relatively low melting eutectic with alumina (unfortunately at the fluorite end of the alumina-fluorite mixture). Fluorite is a very popular ingredient in thermite mixtures for that reason. But cooling a manganese thermite sufficiently simply by slagging it with high amounts of CaF_2 doesn't work because too much of the good stuff interferes with the reaction kinetics, thereby impeding ignition or leading to fizzling mixtures.

The fourth possibility, fairly obvious at first glance, is the use of another manganese oxide, other than manganese (IV) oxide, one for which the reduction reaction yields much less heat than MnO_2 reduction does. Again, this is easier said than done: detailed calculations show that most other oxides of manganese including manganese (III) oxide (Mn_2O_3) and manganese (II, III) oxide (Mn_3O_4) suffer from the same problem as manganese (IV) oxide: the reaction enthalpies of the reductions of these oxides is so high that in adiabatic conditions the mix will run to temperatures that well exceed the boiling point of manganese metal.

That then leaves one oxide, the lower oxide manganese (II) oxide, MnO . For the reduction reaction $\text{MnO} + 2/3 \text{Al} \rightarrow \text{Mn} + 1/3 \text{Al}_2\text{O}_3$ the enthalpy of reaction (at 298 K) is much lower: - 173 kJ (per mol of MnO). Since as the reaction products comprise of 1 mol of Mn and 1/3 mol of Al_2O_3 , the heat needed to melt and heat this mixture to 2,054 C, according to above, is: $85 + 1/3 \times 393 = 216$ kJ.

Since as the heat generated during the reaction (173 kJ) is lower than the heat required to heat the reaction products to the melting point of alumina (216 kJ), this reaction is considered as heat starved and cannot lead to a liquid slag/metal mix and gravitational separation of the metal from the slag. In order to obtain both metal and slag in liquid conditions using the reduction of MnO as a heat source, extra heat has to be applied. There is of course an easy way of doing this: by adding manganese (IV) oxide; the heat of that reduction will be sufficient to reach 2,054 C, without overshooting the target temperature and ending up with boiling manganese metal. A blend of MnO and MnO_2 in the right proportions is therefore called for.

A simple but detailed calculation based on the reaction heats of both reductions and the required heat to heat the reaction products to 2,054 C shows that this optimum, in strictly adiabatic conditions, lies somewhere near a molar ratio of $\text{MnO} / \text{MnO}_2 = 1 / 0.30$ (or a 3.333... ratio). In the formulation, stoichiometry and the use of a fairly high level of CaF_2 were also taken into account and the resulting target formulation expected in adiabatic conditions to produce an end temperature close to 2,054 C is as follows:

MnO 1 mol
 MnO_2 0.3 mol
 Al 1.0666... mol
 CaF_2 0.24 mol

That leaves one 'minor' problem: MnO is not near as readily available as the other manganese oxides. I therefore had to resort to home brewing it, which will be the *subject of a separate post*, by thermal decomposition of manganese (II) carbonate to manganese (II) oxide in the absence of air, according to $\text{MnCO}_3 \rightarrow \text{MnO} + \text{CO}_2$.

A first attempt to light up an 'MnO only' (no MnO_2 at all - as a baseline) showed that the thermite based on manganese (II) oxide alone burns only with great difficulty and very coolly, confirming the low reaction heat on which the new manganese thermite mixture is founded. The slag/metal mix after cooling is of the spongy 'muffin' type with the metal trapped inside in powder form.

A second attempt, using the formulation above in a 20 g batch was already very near successful: the thermite burned well, not very fast but hot enough for the molten slag/metal mix to mostly collect at the bottom of the crucible (I use egg cups for these small developmental reactions). Breaking open the slag heap revealed multiple small manganese reguli, some a few mm across, many about 1 mm and many more sub mm. The metal breaks away clean from the alumina/fluorite slag and reacts very vigorously with strong hydrochloric acid, as chemically it's expected to do.

Reasoning the reaction probably still ran a little too cool, I decided to increase the amount of MnO_2 to *about 0.4 mol*, the formulation then becoming $\text{MnO} = 1$ mol, $\text{MnO}_2 = 0.4$ mol, $\text{Al} = 1.2$ mol, $\text{CaF}_2 = 0.27$ mol and another 20 g test batch was mixed and ignited. Predictably, it ran faster and a little hotter and yielded more and larger globules of manganese metal. Based on the amount of metal recovered yield was still only a measly 25 % but already this is about twice as high as what I previously obtained with the most successful efforts with pure manganese (IV) oxide.

The hunt is now on to further optimise the $\text{MnO} / \text{MnO}_2$ ratio, run larger reactions and obtain better yields. Other thermites show that in open reactor conditions and relatively small batches, yields of 50 % or more can reasonably be expected.

The obtained results so far show conclusively that backyard manganese thermites based on blends of manganese (II) and manganese (IV) oxides can run 'well behaved', without deflagration of the mix or boiling off the metal.

Note: this article is followed up by a report on [manganese thermites based on blends of \$\text{Mn}_2\text{O}_3\$ and \$\text{MnO}\$](#) .